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SUNNYVALE, BLDG. 102, EXT. 27515
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9-8
1962

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AD612962

5-10-62-53

NOVEMBER 1962

OPTICAL AND INFRARED ABSORPTANCE AND EMISSION
PROPERTIES OF SOLID H_2O , CO_2 , N_2 AND O_2 :
AN ANNOTATED BIBLIOGRAPHY, 1958-1962

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SPECIAL BIBLIOGRAPHY

SB-62-59

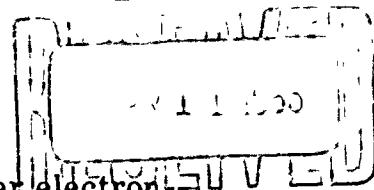
1. Babenko, V. P., et al.
Methods and apparatus for low temperature optical
and spectral studies. PRIBORY I TEK. EKSPT.,
(1), p. 115-120, 1959. (In Russian)

Metallic cryostats designed for studies on the absorption and luminescence of crystals
in the free and stressed state and for photoelectric work at liquid hydrogen and helium
temperatures are described.

2. Bernal, J. D.
The physics of water and ice. Introductory remarks.
ROY. SOC. PROC. v. A247, p. 421-423, Oct 1958.

An introduction to the structure of ice and water.

3. Brocklehurst, B. and Pimentel, G. C.
Thermoluminescence of solid nitrogen after electron
bombardment at 4.2 K. J. CHEM. PHYS. v. 36,
n. 8, p. 2040-6, 15 Apr 1962.



Solid nitrogen annealed at 20°K and then bombarded with electrons at 4°K gives three
glow peaks on warming, at 10°, 14.5°, and 19°K. Unannealed nitrogen gave broader
peaks. A feeble, long-lived glow followed the normal afterglow after bombardment at
4°K. Thermal effects during warming were observed in one apparatus with radiation
shielding at 77°K, but they were not observed in a much more sensitive apparatus with
radiation shielding at 4°K. The thermal effects are probably caused by an anomalous
vapor pressure and loss of Dewar vacuum. The data are discussed with reference to

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two interpretations, the storage of 2D excited nitrogen atoms and the recombination of 4S nitrogen atoms through diffusion. The latter explanation is preferred and a simple model is offered to account for the three diffusion activation enthalpies implied by the three thermo-luminescence peaks.

4. Broida, H. P. and Peyron, M.

Luminescence of solid nitrogen (4. 2°K.) containing atoms or free radicals. Effect of dilution with argon. J. PHYS. RADIUM v. 18, p. 593-5, 1957.

Products obtained from a microwave discharge in nitrogen are rapidly frozen on a glass surface kept at liquid-He temperatures. Metastable atoms are evidently trapped in the solid and able to radiate. Some molecular spectra are probably formed by recombination. Dilution with Ar causes new band systems to appear and some lines are shifted.

5. Broida, H. P. and Nicholls, R. W.

Phosphorescence of nitrogen and nitrogen-argon deposited films at 4. 2°K. J. CHEM. PHYS., v. 32, n. 2, p. 623-4, Feb 1960.

Phosphorescence was induced in nitrogen and nitrogen-argon mixtures (deposited at 4. 2°K after passage through a microwave discharge) by illumination of the deposits with a variety of filtered light sources over the wavelength range 2000-10,000 Å. The spectrum of the phosphorescence contains only the α and α' features of N I at 5230 Å and is interpreted in terms of a restimulation of the green afterglow.

6. Broida, H. P. and Peyron, M.

Luminescence of solid nitrogen (4. 2°K.) containing some atoms or free radicals. Effect of traces of oxygen, hydrogen and water vapor. J. PHYS. RADIUM v. 19, p. 480-484, 1958.

β lines in the solid nitrogen spectrum are attributed to the $^1S-^1D$ transition of atmospheric oxygen. Small amounts of hydrogen and water vapor have no important effects. Satellite lines on each side of the α line from the atmospheric nitrogen transition $^2D-^4S$ and β lines are related to the respective atoms, as well as to the nitrogen molecule. Possibilities of vibrational energy exchanges in the solid are discussed.

7. Dressler, K. and Schnepp, O.
Absorption spectra of solid methane, ammonia,
and ice in the vacuum ultraviolet. J. CHEM.
PHYS. v. 33, n. 1, 270-4, Jul 1960.

The vacuum u.v. spectra of solid ammonia and ice are found to be shifted to higher frequencies relative to the corresponding vapour spectra by 7000 cm^{-1} . The effects of hydrogen bonding in the ground states of these solids, and the nature of repulsive interactions possible in the excited states are discussed.

8. Giguère, P. A. and Harvey, K. B.
An infrared study of hydrogen bonding in solid
 H_2O_2 and $\text{H}_2\text{O}-\text{H}_2\text{O}_2$ mixtures. J. MOLECULAR
SPECTROSCOPY v. 3, p. 36-45, 1959.

Infrared spectra are given for solid H_2O_2 , ice, and H_2S at 80°K . Changes occurred in the spectra of both H_2O and H_2O_2 when these compounds were deposited together. Intermolecular frequencies underwent large downward shifts, while internal vibrations were little affected.

9. Glasel, Jay A.
Near-infrared absorption spectra of ortho- and
para- H_2O in solid xenon and argon. J. CHEM.
PHYS. v. 33, p. 252-5, 1960.

The spectrum of H_2O trapped in a solid Xe matrix at 20°K . approximates the gas spectrum of a mixture of -75% ortho and 25% para H_2O at 20°K . The intensities of the lines of the spectrum change depending on whether Ar, Xe, or N is used as a matrix, and in particular the rotational structure due to the R branch disappears for the N matrix. Other than a constant shift of the frequency of vibration, the rotational spacings are constant from an Ar matrix to a Xe matrix. In a given matrix the intensity pattern of the lines change with the condition of the matrix.

10. Haas, C. and Hornig, D. F.
Inter- and intra-molecular potentials and the
spectrum of ice. J. CHEM. PHYS. v. 32,
n. 6, p. 1763-9, Jun 1960.

While the spectra of H_2O and D_2O ice cannot yet be explained unambiguously, the spectra of HDO in dilute solution in either H_2O or D_2O may be interpreted

readily. In particular, since ν_{OH} occurs at 3275 cm^{-1} and $2\nu_{OH}$ at 6300 cm^{-1} , nearly the harmonic value, the barrier to proton transfer lies well above the latter level and must exceed 23 kcal/mole. The width of ν_{OD} at 2416 cm^{-1} is only 20 cm^{-1} , whereas that of ν_{OH} is about 80 cm^{-1} and $2\nu_{OH}$ about 600 cm^{-1} . These widths can be explained by proton tunnelling if the barrier height is near 32 kcal, in which case the second minimum must lie below the level ν_{OH} . It must therefore be less than 14 kcal/mole above the primary minimum. A doubling of ν_{OD} from OD...OD pairs was also observed and the magnitude of the splitting is consistent with an effective charge of 0.6e on the protons. It is clear from these results that the usual width of hydrogen bonded OH lines is not an intrinsic characteristic of the O-H...O bond but results largely from intramolecular coupling of the O-H motions.

11.

Hoerl, E. M.

The absorption spectrum of solid α -oxygen.

J. MOL. SPECTROSCOPY v. 3, p. 548-549,

1959.

Spectroscopic studies were made of oxygen gas condensed on a cold surface at liquid helium temperatures and irradiated with electrons of 15-20 kv. energy. The wavelength range 2300-8800 Å. was investigated. Between 2400 and 2700 Å. some broad and diffuse bands were found which were in the same spectral region as the Herzberg bands of gaseous oxygen. Other previously reported bands were also studied. Spectra taken after electron bombardment of α -O for periods of 10-90 seconds and at a 100 mw./sq. cm. intensity showed continuous absorption for wave lengths shorter than 3250 Å.

12.

Hornig, D. F., White, H. F. and Reding, F. P.

The infrared-spectra of crystalline H_2O , D_2O ,

and HDO. SPECTROCHIM. ACTA 12, p. 338-49,

1958.

The infrared spectra of normal and deuteriated ice were studied at temperatures down to -190° . No important spectral differences between the various specimens were found. The infrared spectra were compared and the spectrum of crystalline HOD identified. Starting from the HOD spectrum the spectra of H_2O and D_2O could be clarified. The band at 2230 cm.^{-1} in ice is the 2nd overtone of a librational mode. The stretching region of ice consists of $2\nu_2$ at about 3150 cm.^{-1} , ν_3 at about 3240 cm.^{-1} , and ν_1 at about 3350 cm.^{-1} ; D_2O is analogous. The cross-over between the frequency of ν_1 and ν_3 in passing from gas to solid is caused by a change in the stretch-stretch interaction constant. Its magnitude in ice can be roughly explained on electrostatic grounds. The spectrum of the overtone region shows that the barrier to proton transfer in ice is $> 27\text{ kcal./mole}$.

13.

Hotellier, M. N. and Kahane, A.

Variation of the birefringence of ice as a function of temperature. COMPTES RENDUS ACAD. SCI. (FRANCE) v. 254, n. 2, p. 246-8, 8 Jan 1962.
(In French)

The birefringence of small (15 mm thick at 0°C) single crystals of ice was measured parallel to the optic-axis in the temperature range 0° to -195°C. An abnormal variation was found between -100° and -180°C caused by the reorientation of the molecules of water in the crystal.

14.

Jacox, Marilyn E. and Milligan, Dolphus E.

THE INFRARED SPECTRA OF THICK FILMS OF CO₂ AND CO₂ + H₂O AT LOW TEMPERATURES.
Mellon Inst. of Industrial Research, Pittsburgh,
Pa. Rept. no. AFOSR-685, 1 May 61, 14p. ASTIA
AD-256 499.

High resolution infrared absorption studies on thick films of CO₂ and of dilute solid solutions of H₂O in CO₂ have been made at 53 and 4 K. A spectroscopically observable complex between CO₂ and H₂O is not formed. The isolation of H₂O in the CO₂ matrix at 53 K is quite good. Monomer and dimer absorptions have been assigned in the 1/1600 to 1/1650 cm region. In very thick films of pure CO₂ nu(1) appears, weakly, at 53 K. In samples deposited at 4 K the nu(1) absorption is markedly intensified, probably because of an increased number of crystal imperfections, and 2nu(2) is also observed. Similar systems of lattice vibrations have been observed in combination with both nu(2) and nu(3).

15.

Kislovskii, L. D.

Optical properties of water and ice in the infrared and radiowave regions of the spectrum. OPTIKA I SPEKTROSK v. 7, n. 3, p. 311-20, Sep 1959.
(In Russian)

The values of the optical constants (the refractive index n and the absorption factor k) were calculated for water and ice in a wide range of infrared (2.1-3.4 μ) and radiowave (0.01 cm-1000 km) frequencies. The calculations were based on the author's own model. Values of n and k at certain wavelengths, some taken from published work and some determined by the author, were used in these calculations. The calculated dependences of n and k on wavelength are shown graphically; they were found to agree well with experimental results reported by others.

16. Kruger, J. and Ambs, W. J.
Optical measurements on thin films of condensed
gases at low temperatures. J. OPT. SOC. AMER.
v. 49, n. 12, p. 1195-8, Dec 1959.

A determination of the refractive indices of thin films of oxygen, nitrogen, carbon dioxide and water, condensed at 4.2°K was made. These were obtained for the 5461 Å line of Hg with an ellipsometer. Similar measurements were also made on films of these gases condensed after passage through a microwave discharge. With the exception of N₂ and Kr, measurable differences in refractive indices were observed between films condensed from discharged and undischarged gases.

17. Landau, A., Allin, E. J. and Welsh, H. L.
Absorption spectrum of solid oxygen in the wave-
length region from 12,000 Å. to 3300 Å.
SPECTROCHIM. ACTA v. 18, p. 1-19, 1962.
(In English)

The α form of the solid was studied at 21°K. A few results were also obtained for the β and γ forms. The upper states of the electronic systems are A, B, A + A, A + B, B + B, where A = $^1\Delta_g$ and B = $^1\sum_g^+$. The 19 bands studied were different in structure, but profiles showed a sharp red edge with intensity degradation towards the violet. Combination tones of the appropriate molecular frequency are superimposed on a continuous distribution of lattice frequencies. The molecular constants calculated are about the same as those for the free molecule.

18. Lippincott, E. R., Weir, C. E. and Van
Valkenburg, A., Jr.
Infrared studies of dense forms of ice.
J. CHEM. PHYS. v. 32, p. 612-14, 1960.

Infrared patterns at 2-15 μ are included as follows: water at 25° and 1 atm., ice I at -7° and 1 atm., ice at -26° and 9000 atm., and ice at -27° and 3000 atm. At high pressure the hydrogen bonds responsible for the open structure of ice I collapse, and H bonding produces a minor effect on the vibration modes. Presumably, weak H bonds still exist in the dense ice but with an O-H...O angle considerably different from 180°.

19. Mutter, R., Mecke, R. and Luettke, W.
A new infrared absorption spectrum of ice.
Z. PHYSIK. CHEM. v. 19, p. 83--88, 1959.
(In German)

The new spectrum, in contrast to most older investigations, shows sharp bands. A theoretical discussion of the causes for their existence is included.

20. Ockman, N.
The infrared and raman spectra of ice. ADVANCES
IN PHYS, v. 7, p. 199-220, 1958.

Contains a review with a bibliography.

21. Ockman, N. and Sutherland, G. B. B. M.
Infra-red and raman spectra of single crystals
of ice. PROC. ROY. SOC. A v. 247, p. 434-40,
21 Oct 1958.

Of the 7 possible arrangements of the H atoms that have been suggested for ice crystal, only one is excluded by the absence of any dichroism in the infrared absorption spectrum.

22. Pilon, A. M.
Phosphorescence of solid nitrogen. COMPTES
RENDUS ACADEM. SCI. (FRANCE) v. 249, n. 16,
p. 1492-3, 19 Oct 1959. (In French)

Preliminary observations are reported upon the effect of high magnetic fields (40 kg) upon the components α (5229 Å) and α' (5945 Å) of the luminescence from nitrogen deposited at 4.2°K from a microwave discharge. The principal effect is a decrease in intensity of the spectral features. An apparent rotational structure has been noticed in the main line (5945 Å) of the α' feature in some cases. Ten, rather than the commonly reported five, components of the α' feature have been observed (both with and without the field) between 5932 Å and 6017 Å. Line widths are too great to detect a Zeeman effect.

23. Pimentel, G. C.
Low temperature spectral behavior of hydrogen-bonded species. In HYDROGEN BONDING SYMPOSIUM PAPERS. Ljubljana, 1957. Published 1959. p. 107-110.
Review of studies of hydrogen stretching of H-bonded species at 4° - 20°K.

24. Robey, D. H.
Ice in space. J. BRIT. INTERPLANET. SOC, v. 17, p. 205-215, 1960.
Equilibrium temperatures and sublimation rates were determined for solid water and carbon dioxide as a function of distance from the sun and absorptivity. A frozen water sphere at one astronomical unit from the sun, which absorbs all incident radiant energy, develops a steady-state temperature of about 195°K. At the same distance and energy conditions, carbon dioxide develops a steady-state temperature of 108°K. Radius decreases for materials per unit of time do not differ by a factor of ten. For ice, the loss is about 0.4 in./day for 100% incident energy radiation absorption; 0.1 in./day for 50%; and 2×10^{-5} in./day for 7%. A flat transparent sheet of ice one cm. thick would stay at a temperature less than 100 K. at one astronomical unit from the sun and would take about a million years to sublime.

25. Schoen, L. J. and Broida, H. P.
Effect of structure on the spectra emitted by solid nitrogen during electron bombardment. J. MOLECULAR SPECTROSC. v. 5, n. 5, p. 416-19, Nov 1960.
Spectra emitted from solids subjected to electron bombardment at low temperature were found to exhibit a dependence on deposition flow rate. It is shown that the observed changes may be ascribed to the effect of deposition temperature on the structure of the solid.

26. Schoen, L. J. and Rebbert, R. E.
Electrical-discharge-induced luminescence of solids at low temperatures. J. MOL. SPECTROSCOPY v. 3, p. 417-24, 1959.

A method is presented for the initiation and study of luminescence in condensed systems at low temperatures. Light emission was initiated by application of high

voltage (10-20 kv.) directly to the He-cooled surface containing the deposited species. The most convenient source in terms of voltage and power flexibility was the high-voltage d.c. power supply. Typical atomic and molecular spectra are presented: the structure and wave lengths of the β line group attributed to trapped oxygen atoms, and the wave lengths of the A and Vegard-Kaplan band systems are compared in nitrogen and argon matrixes. Ion-electron bombardment of the deposited solid appeared to be the principal mechanism of excitation. The method may be applicable to the production and stabilization of free radical species, and useful for the excitation and analysis of electronic band spectra in the condensed phase.